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WO 03/085026 A1

(54) Title: AROMATIC GLYCOLS AND POLYOOLS, PREPARATION PROCESS AND THEIR USE AS MONOMERS

(57) Abstract: Compounds are described, having the following general formula (A) R(CONH-CHR₁OH)_m (A) and their use as monomers in polymerization and polycondensation reactions.

AROMATIC GLYCOLS AND POLYOLS, PREPARATION PROCESS AND
THEIR USE AS MONOMERS.

The present invention relates to aromatic glycols
10 and/or polyols, the relative use as monomers and the
preparation process.

The state of the art normally describes the use of
aliphatic glycols and/or polyols as co-monomers in the
production of polyester resins, unsaturated polyester
15 resins, thermoplastic polyester resins and polyurethane
resins. It is known however that the introduction of aro-
matic rings in the chains of polyurethane resins or poly-
ester resins enhances the chemical properties of these
structures, such as an improved resistance to corrosion,
20 oxidation with ultraviolet rays, temperatures, etc. and
also allows the physico-mechanical characteristics to be
enhanced. As of today, however, it has only been possible
to insert these aromatic groups in the chains through the
use of pure aromatic polycarboxylic acids in the case of
25 polyester resins or with the use of aromatic isocyanates.

Further evidence of the importance and usefulness of inserting aromatic nucleuses in the chain of polyurethane or polyester resins, is obtained when, by substituting terephthalic acid, whose polycondensation leads to the 5 production of PET (polyethyleneterephthalate) with 2,6-naphthalenedicarboxylic acid, i.e. by introducing two benzene rings into the chain instead of one single ring, a product, PEN (polyethylenenaphthalate) is obtained, which has the following characteristics and properties.

10 PEN has a structure with a rigid double aromatic ring, whose presence in the polymeric chain accounts for many of the improvements which this polymer shows with respect to PET, such as, for example, a greater resistance, a higher thermal stability and improved barrier 15 properties. PEN also has a higher glass transition temperature and a reduced gas permeability. This polymer has found extremely interesting applications in the field of films, fibres, packaging, above all for drinks and food, and is considered as being a product which can have extremely important applications.

The high cost, however, of 2,6-naphthalenedicarboxylic acid is one of the problems (together with problems relating to disposal and mainly recycling) which has so far hindered a full development of this polymer.

25 The importance of finding alternative methods for

inserting aromatic groups in the chains of polyester resins, unsaturated polyester resins, thermoplastic polyester resins and polyurethane resins, is therefore evident.

The identification of alternative methods which allow the insertion, together with aromatic groups or, alternatively, other functional groups such as imine groups or double bonds, into the chains of polyester resins, unsaturated polyester resins, thermoplastic polyester resins and polyurethane resins, is also of general interest.

10 The present invention therefore proposes to overcome the drawbacks present in the known technique.

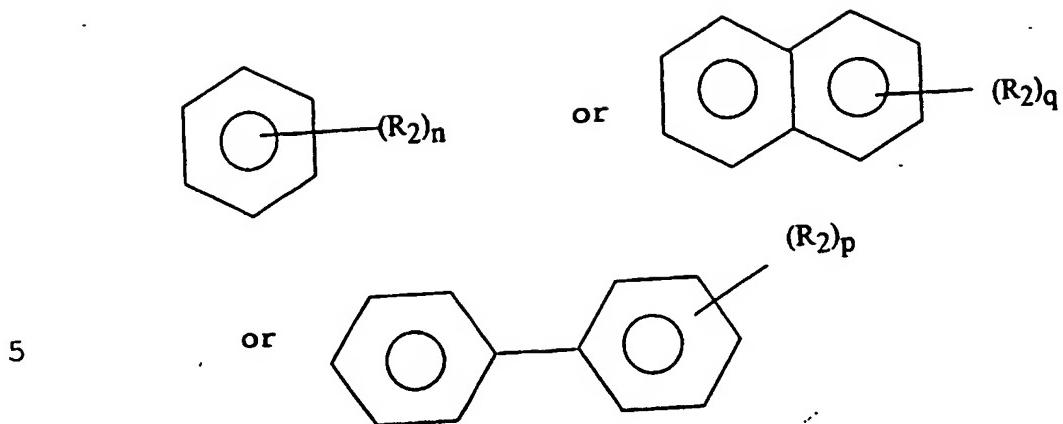
It has been surprisingly found that the aromatic glycols and/or polyols according to the present invention allow various functional groups to be contemporaneously inserted into polyester chains or polymeric chains, in an extremely simple and economically convenient way, and with excellent yields.

In particular, an object of the present invention relates to a compound having the following general formula (A):



wherein:

- R represents a residue obtained by substituting m hydrogen atoms by a compound selected from



or a saturated aliphatic chain, linear or branched,
 having from 2 to 18 carbon atoms or an unsaturated
 10 aliphatic chain, linear or branched, having from 2
 to 18 carbon atoms and with at least one double
 bond;
 wherein R₂, the same or different when n, p or q are
 greater than or equal to 2, represents a linear or
 15 branched alkyl group, having from 1 to 18 carbon at-
 oms;
 n varies from 0 to 4;
 p varies from 0 to 6;
 q varies from 0 to 8;

20 - R₁, the same or different, represents a hydrogen atom, an alkyl group optionally substituted, having from 1 to 6 carbon atoms or an aromatic group op-
 tionally substituted;

- m is equal to 2, 3 or 4.

25 In particular, when R represents a phenyl radical

and m is equal to 2, the substituents -(CONH-CHR₁OH)_m can be in ortho, meta or para position, respectively, preferably in meta or para position.

When R represents a phenyl radical and m is equal to 5 3, the substituents -(CONH-CHR₁OH)_m are preferably in position 1,3,5 or 1,2,4.

In particular, when R represents a phenyl radical and m is equal to 4, the substituents -(CONH-CHR₁OH)_m are preferably in position 1,2,4,5.

10 Preferably, when R represents a naphthalene radical and m is equal to 2, the substituents -(CONH-CHR₁OH)_m are respectively in position 2 and 6.

When R represents a biphenyl radical and m is equal to 2, the substituents -(CONH-CHR₁OH)_m are in para position.
15

m is preferably equal to 2.

n, p and q are preferably equal to 0 or 1.

A further object of the present invention relates to the use of the compound having general formula (A) as 20 monomer in polycondensation and polymerization reactions.

In particular, the compound according to the present invention can be used as monomer in polycondensation and/or polymerization reactions with suitable comonomers to produce saturated and unsaturated polyester resins 25 with aromatic polyacids, polyamide resins, polyurethane

resins or liquid crystal polymers.

A further object of the present invention relates to the polymer obtained by the polycondensation of terephthalic acid with the glycol of 1,4-benzeneddicarboxyamide 5 which has the following structure:



wherein r is greater than or equal to 4.

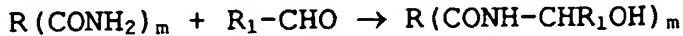
The main advantage of the compound according to the present invention is that it allows the contemporaneous 10 insertion into polyester or polymeric chains of several functional groups, in an extremely simple and economically convenient way, with excellent yields. In particular, the contemporaneous insertion of aromatic rings and -CONH- groups, is particularly advantageous. The -CONH- 15 groups enhance resistance to high temperatures and allow a reduction in the formation of by-products (for example acetaldehyde) of the polymers during the subsequent melting and extrusion.

The insertion of the double bond which allows the 20 hardening of the thermosetting unsaturated polyester resins, is also particularly advantageous.

Another advantage of the polymers obtained by the polycondensation and/or polymerization of the aromatic glycols or polyols according to the present invention is 25 that their properties are such as to allow them to be

used for the production of containers, for example bottles, with an increased impermeability of the wall of the container both from the inside towards the outside of the container (CO_2), and also from the outside towards the 5 inside of the container (O_2), thus allowing it to be used for an improved packaging of carbonated drinks and products sensitive to oxygen such as wines, beer, liquors, soft drinks, food substances.

The compound according to the present invention having general formula (A), is prepared by means of the following reaction:



wherein R, m and R_1 have the meanings previously indicated, and i.e. by reaction of the corresponding amide in 15 a slightly basic solution with the aldehyde suitably substituted at a temperature ranging from 10°C to 180°C, at a pressure ranging from 0 to 15 atm and for a time which varies from 5 minutes to 5 hours.

The reaction is preferably carried out in the presence of a basic anionic resin insoluble in the reaction medium, wherein the reaction medium is water. The temperature preferably varies from 60°C to 120°C.

The pressure is preferably within the range of 2 to 5 atm, whereas the reaction is preferably carried out for 25 a time varying within the range of 20 minutes to 1 hour.

R(-CONH₂)_m is preferably selected from amides of terephthalic acid, isophthalic acid, 2,6-naphthalene-dicarboxylic acid, trimesic acid, pyromellitic acid or trimellitic acid.

5 R₁CHO is preferably selected from formaldehyde and benzaldehyde.

A first application example of the compound according to the present invention is its use as monomer for the production of a thermosetting, unsaturated, or-
10 thophthalic polyester resin.

According to the state of the art, the thermosetting, orthophthalic unsaturated polyester resin is prepared by the reaction of phthalic anhydride with the first comonomer which is propylene glycol and with the second comonomer which is maleic anhydride to have the
15 double bond which forms the bridge with styrene.

With the use of the compound according to the present invention, obtained from the amide of maleic anhydride and the aromatic glycol already containing the
20 functional groups (double bond and aromatic ring), resins are obtained with much better physico-chemical characteristics.

The advantage is that the comonomer (in the case of the resin with phthalic anhydride) is a glycol which, in
25 addition to the presence of the necessary functional

groups, such as the phenyl ring and double bond, and consequently in addition to providing the end-product with the properties associated with the presence of said functional groups, has much lower costs than those of propylene glycol.

The characteristics and advantages of the composition according to the present invention can be better understood with the help of the following detailed and illustrative description.

10 EXAMPLE 1

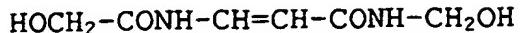
A solution containing 1 mole of maleic diamide equal to 114.07 g in 500 g of methyl alcohol and a solution of 2.05 moles of formaldehyde in the form of a solution in water at 40%, are fed to a static mixer which also acts 15 as heater and the liquid mixture of the two products indicated above is brought to a temperature of 70°C.

The mixture is then directly injected into a reactor containing an anionic resin, Amberliste XE275, the feeding rate of the mixture being regulated so that the residence time is not less than 1.5 minutes and not more than 20 5 minutes.

The mixture thus treated is fed to a fractionation column for the recovery of the methyl alcohol.

The aqueous mixture obtained at the bottom of the 25 fractioning column is extracted with ethyl ether; after

evaporation of the ethyl ether, glycol is obtained



with yields higher than 98%.

EXAMPLE 2

5 A solution containing 1 mole of adipic diamide equal to 144.18 g in 500 g of methyl alcohol and a solution of 2.05 moles of formaldehyde in the form of a solution in water at 40%, are fed to a static mixer which also acts as heater and the liquid mixture of the two products indicated above is brought to a temperature of 70°C.

10 The mixture is then directly injected into a reactor containing an anionic resin, Amberliste XE275, the feeding rate of the mixture being regulated so that the residence time is not less than 1.5 minutes and not more than 15 5 minutes.

The mixture thus treated is fed to a fractionation column for the recovery of the methyl alcohol.

15 The aqueous mixture obtained at the bottom of the fractioning column is extracted with ethyl ether; after evaporation of the ethyl ether, glycol is obtained



with yields higher than 98%.

EXAMPLE 3

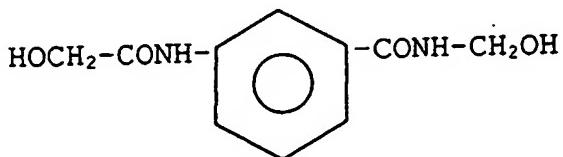
20 A solution containing 1 mole of isophthalic diamide equal to 164.13 g in 500 g of methyl alcohol and a solu-

solution of 2.05 moles of formaldehyde in the form of a solution in water at 40%, are fed to a static mixer which also acts as heater and the liquid mixture of the two products indicated above is brought to a temperature of 5 70°C.

The mixture is then directly injected into a reactor containing an anionic resin, Amberliste XE275, the feeding rate of the mixture being regulated so that the residence time is not less than 1.5 minutes and not more than 10 5 minutes.

The mixture thus treated is fed to a fractionating column for the recovery of the methyl alcohol.

The aqueous mixture obtained at the bottom of the fractionating column is extracted with ethyl ether; after 15 evaporation of the ethyl ether, glycol is obtained



with yields higher than 98%.

WHAT WE CLAIM IS

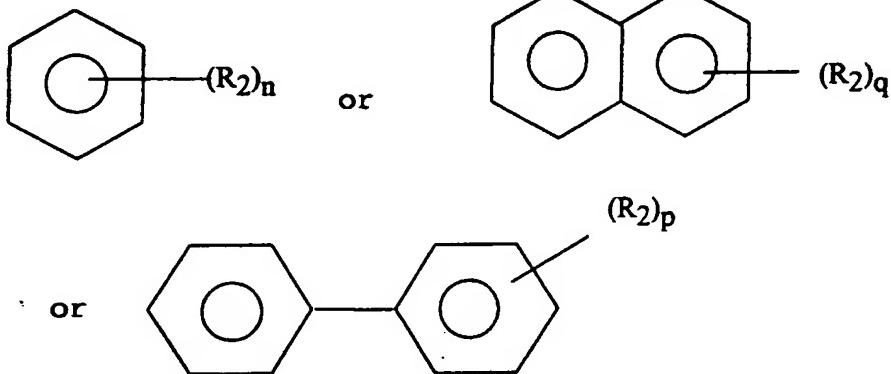
1. A compound having the following general formula (A):



5 wherein:

- R represents a residue obtained by substituting m hydrogen atoms by a compound selected from

10



15

20

or a saturated aliphatic chain, linear or branched, having from 2 to 18 carbon atoms or an unsaturated aliphatic chain, linear or branched, having from 2 to 18 carbon atoms and with at least one double bond;

wherein R_2 , the same or different when n, p or q are greater than or equal to 2, represents a linear or branched alkyl group, having from 1 to 18 carbon atoms;

25

n varies from 0 to 4;

p varies from 0 to 6;

q varies from 0 to 8;

- R₁, the same or different, represents a hydrogen atom, an alkyl group optionally substituted, having from 1 to 6 carbon atoms or an aromatic group optionally substituted;
- m is equal to 2, 3 or 4.

2. The compound according to claim 1, characterized in that, when R represents a phenyl radical and m is equal to 2, the substituents -(CONH-CHR₁OH)_m are in ortho, meta or para position.

3. The compound according to claim 2, characterized in that, the substituents -(CONH-CHR₁OH)_m are in meta or para position.

15 4. The compound according to claim 1, characterized in that, when R represents a phenyl radical and m is equal to 3, the substituents -(CONH-CHR₁OH)_m are in position 1,3,5 or 1,2,4.

5. The compound according to claim 1, characterized in that, when R represents a phenyl radical and m is equal to 4, the substituents -(CONH-CHR₁OH)_m are in position 1,2,4,5.

20 6. The compound according to claim 1, characterized in that, when R represents a naphthalene radical and m is equal to 2, the substituents -(CONH-CHR₁OH)_m are in posi-

tion 2 and 6.

7. The compound according to claim 1, characterized in that, when R represents a biphenyl radical and m is equal to 2, the substituents -(CONH-CHR₁OH)_m are in para position.

8. The compound according to claim 1, characterized in that m is equal to 2.

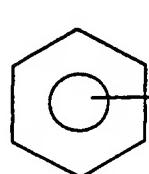
9. The compound according to claim 1, characterized in that n, p and q are equal to 0 or 1.

10 10. Use of the compound having the following general formula (A)



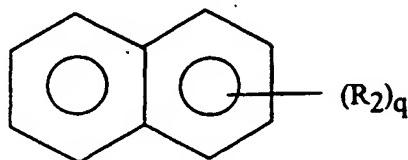
wherein:

- R represents a residue obtained by substituting m hydrogen atoms by a compound selected from



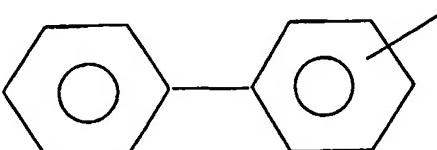
(R₂)_n

or



(R₂)_q

20
or



(R₂)_p

20

or a saturated aliphatic chain, linear or branched, having from 2 to 18 carbon atoms or an unsaturated

aliphatic chain, linear or branched, having from 2 to 18 carbon atoms and with at least one double bond;

wherein R₂, the same or different when n, p or q are greater than or equal to 2, represents a linear or branched alkyl group, having from 1 to 18 carbon atoms;

n varies from 0 to 4;

p varies from 0 to 6;

q varies from 0 to 8;

- R₁, the same or different, represents a hydrogen atom, an alkyl group optionally substituted, having from 1 to 6 carbon atoms or an aromatic group optionally substituted;

- m is equal to 2, 3 or 4

as monomer in polycondensation and polymerization reactions.

11. Use of a compound according to one of the claims from 2 to 9 as monomer in polycondensation and polymerization reactions.

12. The use according to claim 10, wherein the polycondensation and/or polymerization reactions are reactions with the corresponding comonomers to produce saturated or unsaturated polyester resins with aromatic polyacids, polyamide resins, polyurethane resins, liquid crystal

resins or polymers, PET.

13. A polymer which can be obtained by the polycondensation of terephthalic acid with the glycol of 1,4-benzeneddicarboxyamide having the following structure

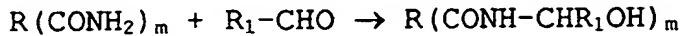
$$H - [O-CO-C_6H_4-CO-O-CH_2-NH-CO-C_6H_4-CO-NH-CH_2]_r-OH$$

wherein r is greater than or equal to 4.

14. Use of the polymer according to claim 13 for the production of packaging containers.

15. Use of the polymer according to claim 13 for the
10 production of packaging containers for carbonated drinks
and products sensitive to oxygen such as wines, beer,
liquors, soft drinks, food substances.

16. A process for the preparation of the compound ac-
cording to one of the claims from 1 to 9, according to
15 the following reaction



wherein R , m and R_1 have the meanings previously indicated, in a slightly basic solution

at a temperature ranging from 10°C
20 to 180°C, at a pressure ranging from 0 to 15 atm and for
a time which varies from 5 minutes to 5 hours.

17. The process according to claim 16, characterized in
that the reaction is carried out in the presence of a ba-
sic anionic resin insoluble in the reaction medium,
25 wherein the reaction medium is water.

18. The process according to claim 16, characterized in that the temperature varies from 60°C to 120°C.

19. The process according to claim 16, characterized in that the pressure is within the range of 2 to 5 atm.

5 20. The process according to claim 16, characterized in that the reaction is carried out for a time varying from 20 minutes to 1 hour.

21. The process according to claim 16, characterized in that R(-CONH₂)_m is selected from amides of terephthalic
10 acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, trimesic acid, pyromellitic acid or trimellitic acid.

22. The process according to claim 16, characterized in that R₁CHO is selected from formaldehyde or benzaldehyde.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/03665

A. CLASSIFICATION OF SUBJECT MATTER				
IPC 7	C08G63/685	C07C235/74	C07C235/76	C07C235/84

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 929 731 A (LEMAN MUSTAFA KYZY VOLKOVA ET AL.) 30 December 1975 (1975-12-30) claims; examples 22-27 ---	1-3,8-12
X	CHEMICAL ABSTRACTS, vol. 27, no. 18, 20 September 1933 (1933-09-20) Columbus, Ohio, US; abstract no. 4698, GEORG WALTER ET AL.: "Resins from Aryl Sulfonamido Carboxylic Acid Amides and the Products Obtained from Aryl Dicarboxylic Acid Amides" page 4698; XP002230159 page 4698, line 17 - line 24 & KOLLOID-BEIHEFTE, vol. 37, - 1933 pages 378-384, ---	1-4,8,9, 16-22

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the International search

18 August 2003

Date of mailing of the International search report

28/08/2003

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/03665

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 02 326 B (FARBENFABRIKEN BAYER) 14 February 1957 (1957-02-14) example 5 ---	1
X	US 2 364 737 A (FRANK CLIFTON MCGREW) 12 December 1944 (1944-12-12) claims; examples I,,III-V ----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 03/03665

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DE 1002326	B	14-02-1957	NONE			
US 2364737	A	12-12-1944	NONE			